Mechanisms of catalytic ozonation: An investigation into superoxide ion radical and hydrogen peroxide formation during catalytic ozonation on alumina and zeolites in water

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ARTICLE INFO

ABSTRACT

This study aims to investigate mechanisms of ozonation in the presence of ZSM-5 zeolites and γ-alumina in water. Four ZSM-5 zeolites with varying silica to alumina ratios and with both hydrogen and sodium counter ions were used in the study (Z1000H:SiO_2/Al_2O_3 = 1000, Z900Na:SiO_2/Al_2O_3 = 900, Z25H:SiO_2/Al_2O_3 = 25 and Z25Na:SiO_2/Al_2O_3 = 25). The formation of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) and superoxide ion radical ($^oO_2{}^-$) was investigated during ozonation in the presence of ZSM-5 zeolites and alumina using amplex red and 4-chloro-7-nitrobenzo-2-oxa-1,3-dizole (NBD-Cl) as probe molecules. To the authors' knowledge, this is the first report utilising NBD-Cl and amplex red to study mechanisms of catalytic ozonation. The results showed that alumina promotes much higher formation of ROS in aqueous solutions when compared to ozonation alone and ozonation in the presence of ZSM-5 zeolites. The process was found to be pH dependent. Furthermore, alumina showed its highest activity at a pH close to its point of zero charge. The presence of tertiary butyl alcohol (TBA) and phosphates in the reaction solution did not have a significant effect on ROS production in the presence of ZSM-5 zeolites. However, in the case of alumina, the presence of phosphates significantly lowered ROS formation. This indicates the critical importance of surface hydroxyl groups of alumina in ozone decomposition and ROS formation. In contrast to H_2O_2 formation, TBA did not have a significant effect on $^oO_2{}^-$ production in the case of alumina. This suggests that $^oO_2{}^-$ plays a significant role in the formation of hydroxyl radicals. Furthermore, both zeolites and alumina were found to catalyse the removal of NBD-Cl from aqueous solution. Therefore, it is suggested that alumina operates through a radical mechanism leading to the production of ROS. On the other hand, zeolites serve as reservoirs of ozone and adsorbents of organic compounds, which interact via direct ozonation pathways. The activity of zeolites depends on the silica to alumina ratios of the zeolite and is independent of the nature of the zeolite counter ions.

1. Introduction

Catalytic ozonation is a promising technology for the effective removal of pollutants that are resistant to conventional water treatment [1]. However, the mechanisms of these processes are still unclear [2,3]. One of the important questions is whether the catalyst decomposes aqueous ozone leading to the production of reactive oxygen species (ROS) or direct attack of ozone is responsible for the degradation of organic compounds; further investigations are required to find out the different reactive oxygen species and their role in the decomposition of organic pollutants. Therefore, it is important to investigate the formation of ROS in catalytic ozonation.

Ozone in water is unstable and undergoes reactions with water matrix components. The decomposition of ozone in water leads to the formation of ROS, which include the super oxide ion ($^oO_2{}^-$), hydroxyl radicals (^oOH) and hydrogen peroxide (H_2O_2), etc. The formation of ROS in aqueous solution is pH dependent and the production of super oxide ion and hydrogen peroxide increases with the increase of pH [4,5].

The superoxide ion is an important and short-lived entity, constituting the fundamental part of AOPs. Hence the formation of superoxide ion may give the relevant information on the radical reactions taking place. H_2O_2 is also an important ROS since it is the only stable active oxygen species in the AOPs. Furthermore, hydrogen peroxide is one of the most important oxidants and is often

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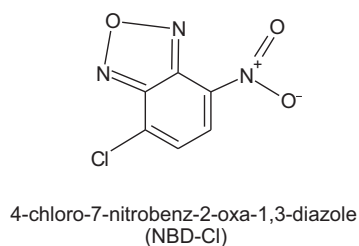   E-mail address: b.kasprzyk-hordern@bath.ac.uk (B. Kasprzyk-Hordern).

4-chloro-7-nitrobenz-2-oxa-1,3-diazole
(NBD-Cl)

Fig. 1. Structure of NBD-Cl.

used as an agent to generate hydroxyl radicals in advanced oxidation processes [6]. Hydrogen peroxide also acts as a hydroxyl radical scavenger and is generated by the combination of two hydroxyl radicals [4]. Thus the measurement of $^oO_2^-$ and H_2O_2 concentrations is useful to evaluate and analyse AOP mechanisms.

The formation of superoxide ion radical ($^oO_2^-$) in catalytic ozonation on modified FeOOH has been reported by Zhang et al. [7]. It was hypothesised that the reaction of ozone with the surface hydroxyl groups of FeOOH leads to the formation of $^oO_2^-$ anion and hydroxyl radicals [7]. Ernst et al. [8] hypothesised that $^oO_2^-$ may form in catalytic ozonation on alumina leading to the generation of hydroxyl radicals; however, no proof of the formation of superoxide ion radical was provided in this investigation.

The formation of H_2O_2 in catalytic ozonation has been reported by some authors and was observed during aqueous ozone decomposition on granular activated carbon [9] and catalytic ozonation of nitrobenzene on modified ceramic honeycomb [10]. Alvarez et al. [9] reported that H_2O_2 formed in ozonation on granular activated carbon was due to the interaction of ozone with the surface of the catalyst. However, Zhao et al. [10] reported that the formation of H_2O_2 in catalytic ozonation of nitrobenzene on ceramic honeycomb was due to the reactions of adsorbed O_3 and nitrobenzene. Furthermore, H_2O_2 formation was higher in catalytic ozonation when compared with ozonation alone [10]. The formation of H_2O_2 in the presence of ZSM-5 zeolites has also been reported [11]. However, hydrogen peroxide was found to be formed at lower concentrations when compared to ozonation alone [11].

The $^oO_2^-$ and H_2O_2 have been determined by various methods in aqueous and biological systems. In this research 4-chloro-7-nitrobenz-2-oxa-1,3-diazole (NBD-Cl) and amplex red were used as probe molecules to detect $^oO_2^-$ and H_2O_2 in the presence of alumina and ZSM-5 zeolites with different silica to alumina ratios (Z1000H:SiO_2/Al_2O_3 = 1000, Z900Na:SiO_2/Al_2O_3 = 900, Z25H:SiO_2/Al_2O_3 = 25 and Z25Na:SiO_2/Al_2O_3 = 25). NBD-Cl [12,13] and amplex red [14–16] have been used before as effective probes in aqueous systems and biological assays. The reason to select NBD-Cl and amplex red (Figs. 1 and 2) as probes had been due to their selective reaction with $^oO_2^-$ and H_2O_2, respectively, leading to the formation of the fluorescent products which can be detected at low levels by fluorescence spectroscopy [12–16]. Based on previous reports it is assumed that other ROS do not interfere with their reactions to produce fluorescent products [12–16].
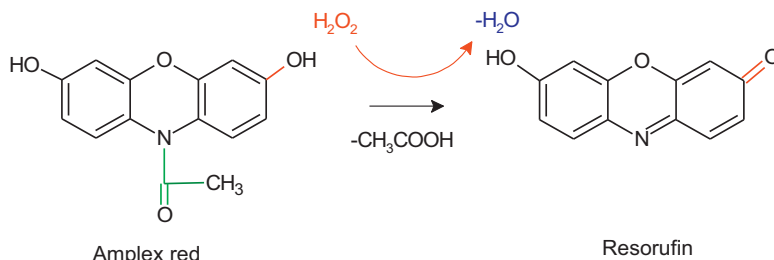
Alumina has been reported by several authors as an effective ozonation catalyst [2,3,17–19]. However, some reports indicate a lack of catalytic activity [20–22]. Recently, high silica zeolites have also been tested as catalysts and were found to be good adsorbents of ozone [23]. They have been successfully applied as heterogeneous catalysts for the ozonation of certain organic pollutants including phenol, *n*-hexadecane and trichloroethene. However, it was assumed that zeolites act mainly as adsorbents of ozone [24–26].

This paper is the first to report the application of NBD-Cl and amplex red in mechanistic studies of catalytic ozonation and reports advances in the research conducted by our group on the understanding of mechanisms of catalytic ozonation on alumina and zeolites. Our previous paper concerned an investigation into hydroxyl radicals' formation in catalytic ozonation of coumarin in water. Enhanced formation of hydroxyl radicals was observed during ozonation over alumina [27]. On the other hand ozonation in the presence of ZSM-5 zeolites did not lead to the formation of hydroxyl radicals. Based on the previous work it is expected that ZSM-5 zeolites may not promote other ROS formation. However, it is important to seek a confirmation because different pathways of reaction mechanisms have been previously proposed. Additionally, in order to investigate the reaction pathways of ozone decomposition in the presence on alumina, it is important to verify the formation and importance of all relevant reactive oxygen species. Furthermore, NBD-Cl removal studies may further help to understand reactions in the presence of ZSM-5 zeolites. This paper aims to add to the understanding of mechanisms occurring during catalytic ozonation through a study of $^oO_2^-$ and H_2O_2 formation.

2. Experimental

2.1. Materials and reagents

The γ-alumina used in this work was supplied by Alcoa, Inc. (USA) and ZSM-5 zeolites were obtained from Zeochem (Switzerland). Information on the properties of zeolites including surface area and pore size data was provided by the manufacturer (Zeochem Switzerland Pvt. Ltd.) or by our group in previous work [21,27]. Amplex red/peroxidise assay, hydrogen peroxide (30% solution in water), NBD-Cl and potassium superoxide (KO_2) were obtained from Sigma–Aldrich. All the chemicals used were of analytical grade and were used without further purification. All the experiments were undertaken with ultrapure deionised water.

2.2. Ozonation experiments

Ozonation experiments to study the formation of $^oO_2^-$ were conducted in the presence of NBD-Cl in a semi-batch reactor [27] at temperature 25 °C. The aqueous solution (190 mL) of NBD-Cl (20 ppm) was transferred to the reactor containing 2.0 g of the catalyst and was subsequently stirred (at 200 rpm) over a
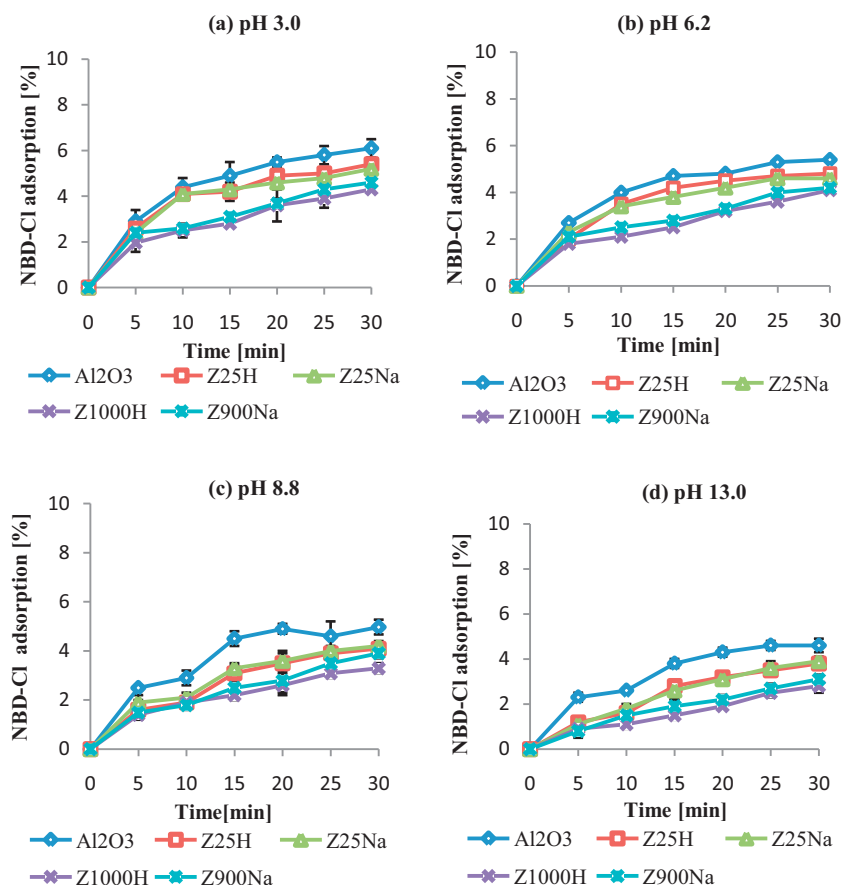
Fig. 2. Formation of resorufin in the reaction of amplex red with hydrogen peroxide.

Fig. 3. Removal of NBD-Cl by adsorption on ZSM-5 zeolites and alumina ($C_{o\,(NBD-Cl)}$ = 20 mg/L; T = 25 °C; pH = 3.0, 6.2, 8.8 and 13.0; catalyst amount = 2.0 g; V = 190 mL; SD ± 0.5%).

period of 30 min. Ozone generated from pure oxygen using a laboratory ozone generator (HTL-500GE/20, Azon Ltd., Canada) was continuously bubbled into the semi-batch reactor containing aqueous solution of NBD-Cl (20 ppm), by means of a ceramic sparger (flow rate: 0.6 mg/min). Samples were collected at 5 min intervals, quenched with 0.025 M Na_2SO_3 in order to remove any residual ozone and were filtered (PTFE 0.45 μm syringe filter). After filtration 1 mL of the sample was immediately added to 2 mL of acetonitrile [12] and immediately analysed with F-4500 Fluorescence Spectrometer (Hitachi, Japan). All the experiments were performed in triplicate, in the dark (reactor was covered by alumina foil during the experiments). The solution pH was adjusted with HCl or NaOH.

Ozonation experiments to investigate the formation of H_2O_2 were conducted at 25 °C in a semi-batch mode (Fig. 3) as discussed above (but without the addition of NBD-Cl). In this investigation 1 mL of the ozonated sample was immediately added to 3 mL of the solution of amplex red (20 mg/L), left for 30 min (optimum time of H_2O_2 reaction with amplex red) and then analysed with F-4500 Fluorescence Spectrometer (Hitachi, Japan). It is important to note that in this work ozone has not been quenched with 0.025 M Na_2SO_3 because Na_2SO_3 can also react with H_2O_2 and this would affect results.

The ozonation experiments in the presence of tertiary butyl alcohol (TBA) and phosphates were performed as described above by adding either TBA or Na_2HPO_4 (50 mg/L) to a semi-batch reactor and following the procedure described above.

In order to understand the effect of catalyst dose on the efficiency of hydrogen peroxide and superoxide ion radical formation HZSM-5 (Z1000H and Z25H) and alumina were selected. Experiments were performed by using 2–8 g of catalysts in the semi-batch

(190 mL water) reactor. The ozonation procedure is discussed above.

2.3. Adsorption experiments

The adsorption experiments aiming to determine the extent to which NBD-Cl was removed by adsorption on the catalysts were performed in the semi-batch mode. For these measurements 2 g of the catalysts were added to 190 mL of NBD-Cl (20 mg/L) solution in a semi-batch reactor and were continuously stirred for 30 min at 200 rpm. Experiments were performed at 25 °C temperature and samples were collected every 5 min.

2.4. Analytical procedures

2.4.1. Analysis of NBD-Cl
The NBD-Cl concentration was measured through absorption of UV–vis light at 342 nm (UV-160A UV–visible spectrophotometer, Shimadzu, Japan) in 1.0 cm cell following the filtration of the working solution, and using a suitable calibration curve. The limits of detection and quantification of the method were 0.07 mg/L and 0.15 mg/L, respectively. The %RSD was less than 5%.

2.4.2. Analysis of NBD-Cl Product
An identification of the NBD-Cl product (reaction product of superoxide ion and NBD-Cl [12,13]) was conducted by recording fluorescence emission spectrum (excited at 470 nm) with F-4500 Fluorescence Spectrometer (Hitachi, Japan) at 550 nm [12]. Both the emission and excitation slits were set to 5.0 nm during the measurements. The formation of NBD-Cl product was confirmed by reacting KO_2 (source of superoxide) and NBD-Cl. The amount of
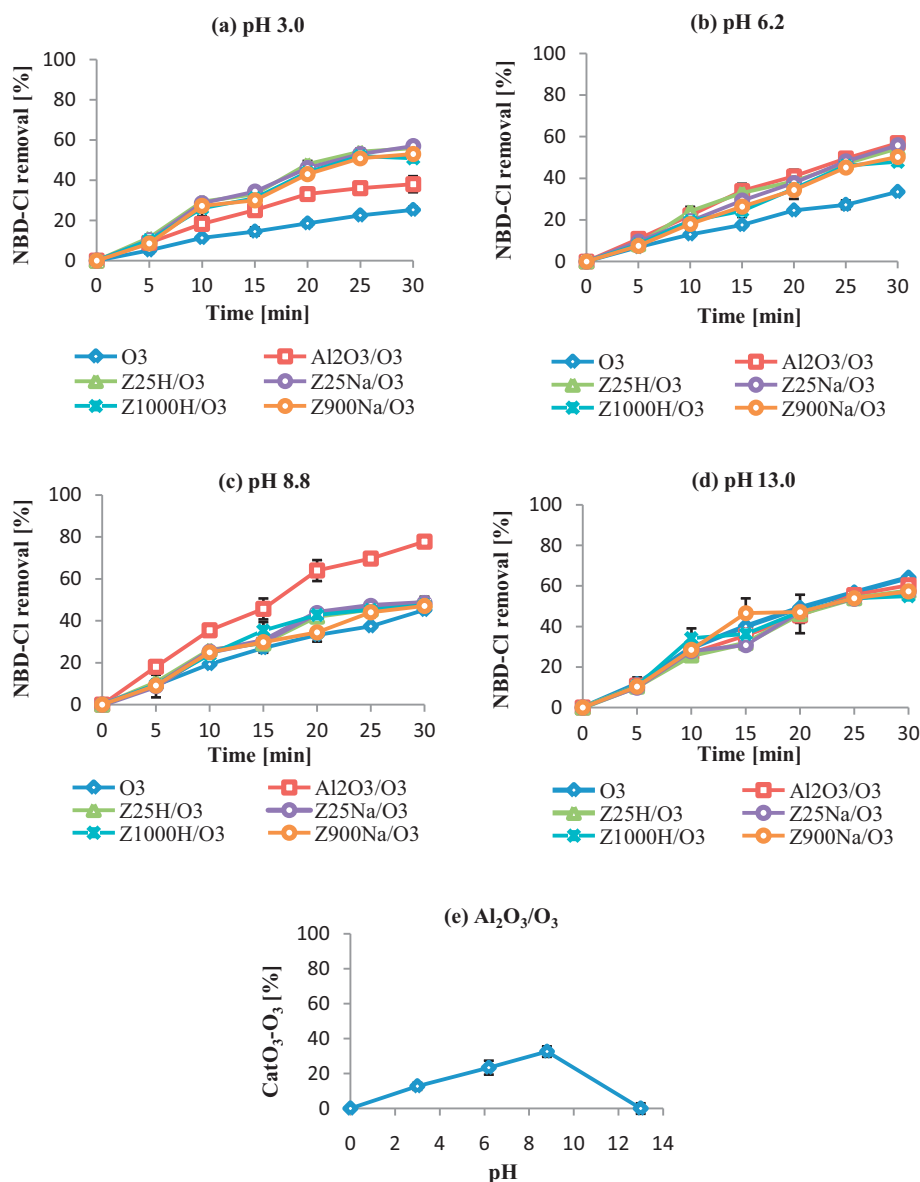
Fig. 4. Removal of NBD-Cl by alumina and zeolites, $C_{o\,(NBD-Cl)} = 20$ mg/L; $T = 25\,°C$; pH = 3.0, 6.2, 8.8 and 13.0; $T = 30$ min; $O_3 = 0.6$ mg/min; catalyst = 2 g; $V = 190$ mL; SD ± 4%.

superoxide ion radical was quantified by plotting fluorescence at 550 nm against $^oO_2^-$ concentration (using 20 mg/L of NBD-Cl and different concentrations of KO_2 that are in the range of 0–7.11 mg/L) [12,13]. All the aqueous samples (1 mL) were mixed with acetonitrile (2 mL) prior to the analysis on fluorescence spectrometer [12]. All the samples were filtered (PTFE 0.45 μm syringe filter) prior to the analysis. The limits of detection and quantification were found to be 2.4 μg/L and 14.4 μg/L, respectively. The %RSD was less than 5%.

In order to investigate the interference due to H_2O_2, experiments have been performed by reacting 1 mL of H_2O_2 (20 mg/L) with 1 mL of NBD-Cl (20 mg/L) for 1 h.

2.4.3. Analysis of resorufin

The concentration of H_2O_2 was determined from the fluorescence emission spectrum (excited at 563 nm) of resorufin by using F-4500 Fluorescence Spectrometer (Hitachi, Japan). Both the emission and excitation slits were set to 5.0 nm. Fluorescence at 587 nm was recorded [14] and the calibration curves were established by

reacting hydrogen peroxide (concentration ranges 0–170 μg/L of H_2O_2 prepared from 30% aqueous solution of H_2O_2) with amplex red reagent (20 mg/L) for 30 min. Due to the fact that amplex red reaction with H_2O_2 is pH dependent, calibration curves were established at different pH values: 6.2, 8.8 and 13. The limits of detection and quantification were determined for H_2O_2 by signal to noise approach and were found to be 5 μg/L and 12 μg/L, respectively. The %RSD was less than 5%.

2.4.4. Analysis of ozone dose

The ozone concentrations were measured with an iodometric method [28]. In-gas and off-gas were continuously introduced to two set of glass bottles, each filled with 200 mL of 2% KI, through a ceramic sparger (Fig. 3). After acidification with 10 mL of 1 N HCl, the liberated iodine was titrated with standard 0.005 N $Na_2S_2O_3$ using a starch indicator.

2.4.5. Analysis of phosphates

The concentration of phosphates was determined by means of ion chromatography using a DIONEX DX-120 system with Ion Pac
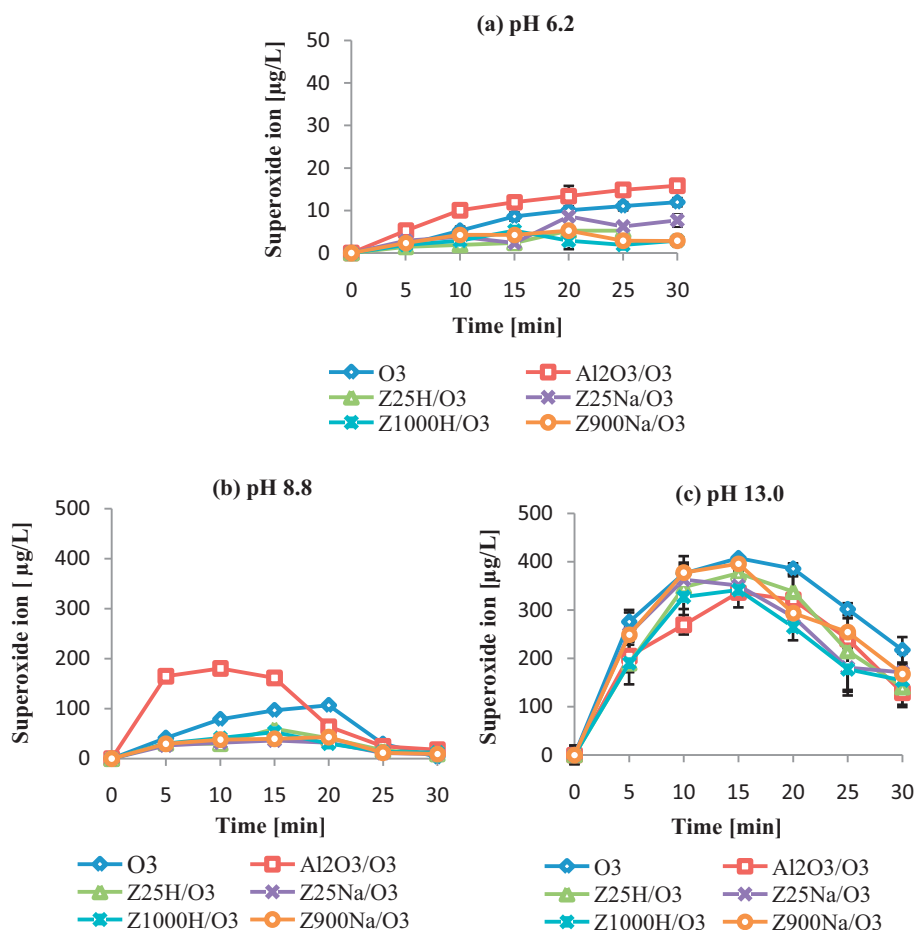
(a) pH 6.2

O3   Al2O3/O3
Z25H/O3   Z25Na/O3
Z1000H/O3   Z900Na/O3

(b) pH 8.8

O3   Al2O3/O3
Z25H/O3   Z25Na/O3
Z1000H/O3   Z900Na/O3

(c) pH 13.0

O3   Al2O3/O3
Z25H/O3   Z25Na/O3
Z1000H/O3   Z900Na/O3

Fig. 5. Formation of superoxide ion radical in the ozonation of NBD-Cl ($C_{o\,(NBD-Cl)}$ = 20 mg/L; T = 25 °C; pH = 6.2, 8.8 and 13.0; O_3 = 0.6 mg/min; catalyst = 2.0 g; V = 190 mL; excitation wavelength = 470 nm; emission wavelength = 550 nm; SD ± 5 μg/L).

As14 analytical column (4 mm × 250 mm) and Ion Pac AG14 guard column (4 mm × 250 mm) coupled with an ED-50A electrochemical detector (Dionex, USA). Analyses were performed at a flow rate of 0.82 mL/min. The injection volume of the sample was 25 μL. The calibration curve was established before analysis. The limit of detection was 0.5 mg/L. The %RSD for all analysed phosphate samples was less than 5%.

3. Results and discussion

3.1. Removal of NBD-Cl and formation of superoxide anion radical

3.1.1. Adsorption of NBD-Cl on zeolites and alumina

The adsorption data is shown in Fig. 3 as the percentage of total NBD-Cl concentration removed from the solution with time at various pHs. The data shows that alumina revealed higher adsorption capacity than zeolites. The adsorption of NBD-Cl on all catalysts was found to be very low. For example only about 4–5% (0.4–0.5 mg/g) of NBD-Cl was adsorbed on 2 g of alumina within 30 min contact time at studied pH values (3.0, 6.2, 8.8 and 13) as shown in Fig. 3. Furthermore, the zeolites with higher alumina content (Z25H and Z25Na) had slightly higher adsorption when compared with high silica zeolites (Z1000H and Z900Na). For example about 4% (0.4 mg/g) of NBD-Cl was adsorbed on Z25H and Z25Na at all studied pH values. However, only 3–3.5% (0.3–0.35 mg/g) of NBD-Cl was adsorbed on Z1000H and Z900Na (Fig. 3). The data for experiments carried out at different pH values shows that the adsorption of NBD-Cl decreases to some extent at basic pH. It may be because the surface is fully populated with OH⁻ ions at this pH

and this phenomenon might result in the decrease of adsorption of NBD-Cl.

3.1.2. Catalytic ozonation of NBD-Cl and the effect of pH

In the present investigation experiments have been performed at pH values 3.0, 6.2, 8.8 and 13.0. The data in Fig. 4 shows the percentage removal of NBD-Cl with time. The data clearly indicates that (Fig. 4) catalytic ozonation of NBD-Cl in the presence of alumina shows higher removal of NBD-Cl when compared with ozonation alone at pH values 3.0, 6.2 and 8.8 (Fig. 4). The percentage removal of NBD-Cl in the case of ozonation in the presence of alumina has been found to increase with the increase in pH and was the highest near point of zero charge of alumina (pH$_{PZC}$) as shown in Fig. 4e. For example at pH 8.8 the NBD-Cl removal was 30% higher than ozonation alone (Fig. 4e). This is in contrast with the ozonation in the presence of ZSM-5 zeolites. In the case of ZSM-5 zeolites the NBD-Cl removal efficiency (the percentage difference between catalytic ozonation on zeolites and ozonation alone) decreased with the increase in pH of the solution (Fig. 4), which indicates that ozonation in the presence of ZSM-5 zeolites may follow a different mechanism than that of ozonation in the presence of alumina. Additionally, the experiments revealed that all studied catalysts were ineffective during the ozonation at pH 13 (had similar removal of NBD-Cl when compared with ozonation alone (Fig. 4d)). This may be due to the high concentration of OH⁻ ions that are responsible for high rates of aqueous ozonation decomposition at pH 13 [27]. The low catalytic activity of alumina at pH 13 may be due to changes in its surface properties. As discussed before, at pH 13 the surface of alumina does not have protonated
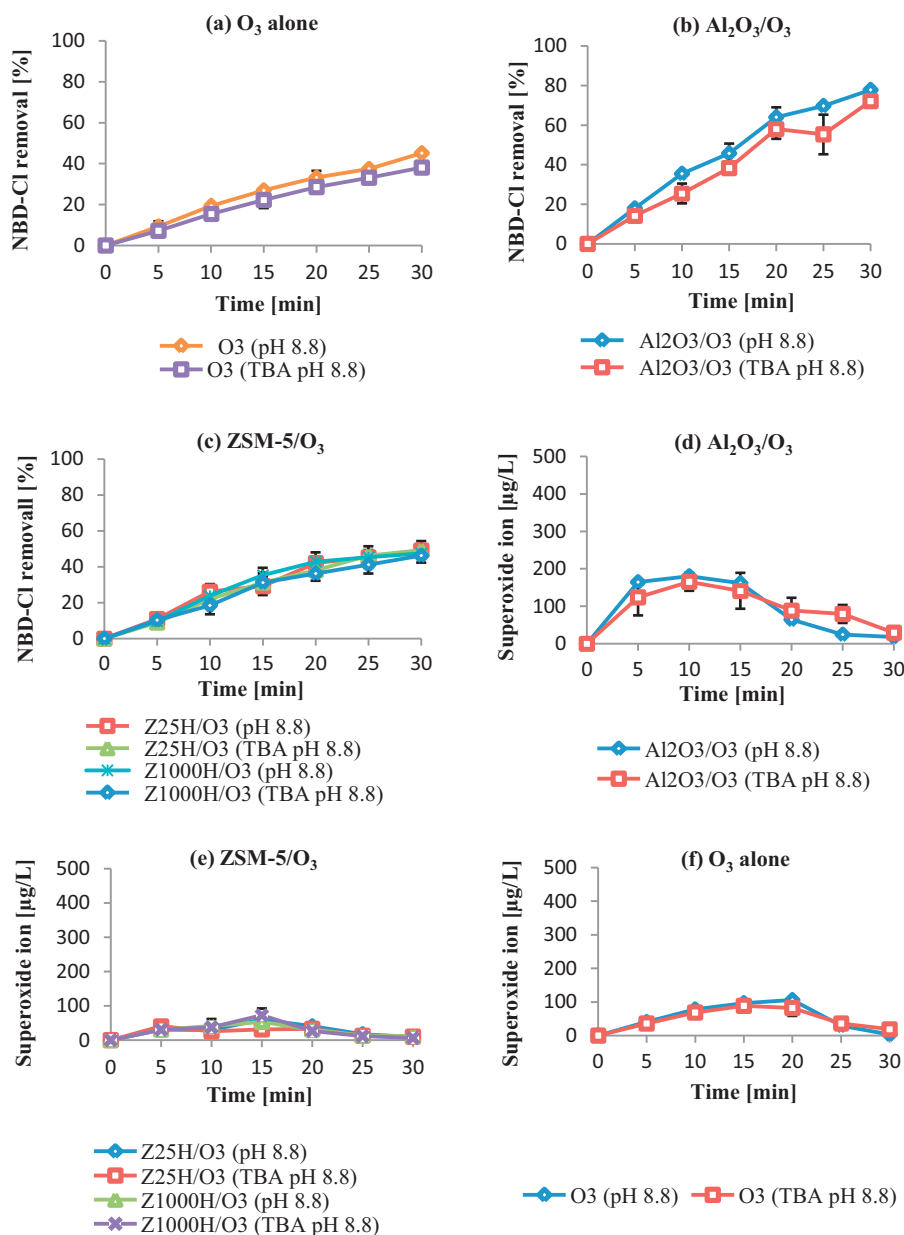
Fig. 6. Effect of TBA on the removal of NBD-Cl and formation of super oxide ion in O_3, Al_2O_3/O_3 and ZSM-5/O_3 ($C_{o\,(NBD-Cl)}$ = 20 mg/L; O_3 = 0.6 mg/min; T = 25 °C; pH = 8.8; TBA = 50 mg/L; catalyst = 2.0 g; V = 190 mL; SD ± 5).

surface hydroxyl groups, which are believed to be responsible for ozone decomposition [18]. It is also worth noting that the pH of the solution did not change significantly (±0.1) after 30 min ozonation with and without catalysts.

3.1.3. The formation of superoxide ion radical and the effect of pH

The formation of superoxide ion radical has been monitored during the ozonation of NBD-Cl. The results clearly indicated that the formation of $^oO_2^-$ in the presence of alumina was the highest at pH = 8.8 (pH = pH$_{PZC}$) when compared with ozonation alone (Fig. 5b). It is important to note that during the first 10–15 min the $^oO_2^-$ formation rate increased and after about 15–20 min it decreased (Fig. 5b). This may be due to the reaction of NBD-Cl product with ozone and other oxidising species present in the system. Additionally, NBD-Cl may be adsorbed on the catalyst surface. It is interesting to note that there was no significant fluorescence at pH = 3.0. This may be because of low yields of $^oO_2^-$ as its formation is higher at basic pH value [5]. In contrast to Al_2O_3/O_3, the ZSM-5

zeolites did not show significantly higher fluorescence when compared with ozonation alone at all pH values (Fig. 5). This leads to the conclusion that ozonation in the presence of ZSM-5 zeolites does not result in the formation of superoxide ion radicals. It is important to note that significantly higher $^oO_2^-$ was observed at pH 13 in all studied ozonation systems (Fig. 5c). This may be due to the presence of high concentration of OH$^-$ ions in the solution at this pH value that lead to the high aqueous ozone decomposition and formation of super oxide ion radical [5].

The experiments to see the interference due to H_2O_2 indicated that H_2O_2 does not react with NBD-Cl to produce fluorescence product and similar results have been reported by other researchers [12]. Furthermore, the interference due to hydroxyl radicals can be investigated by TBA effect.

3.1.4. Effect of hydroxyl radical scavengers

The ozonation experiments have been performed in the presence of tertiary butyl alcohol (TBA) in order to understand the role
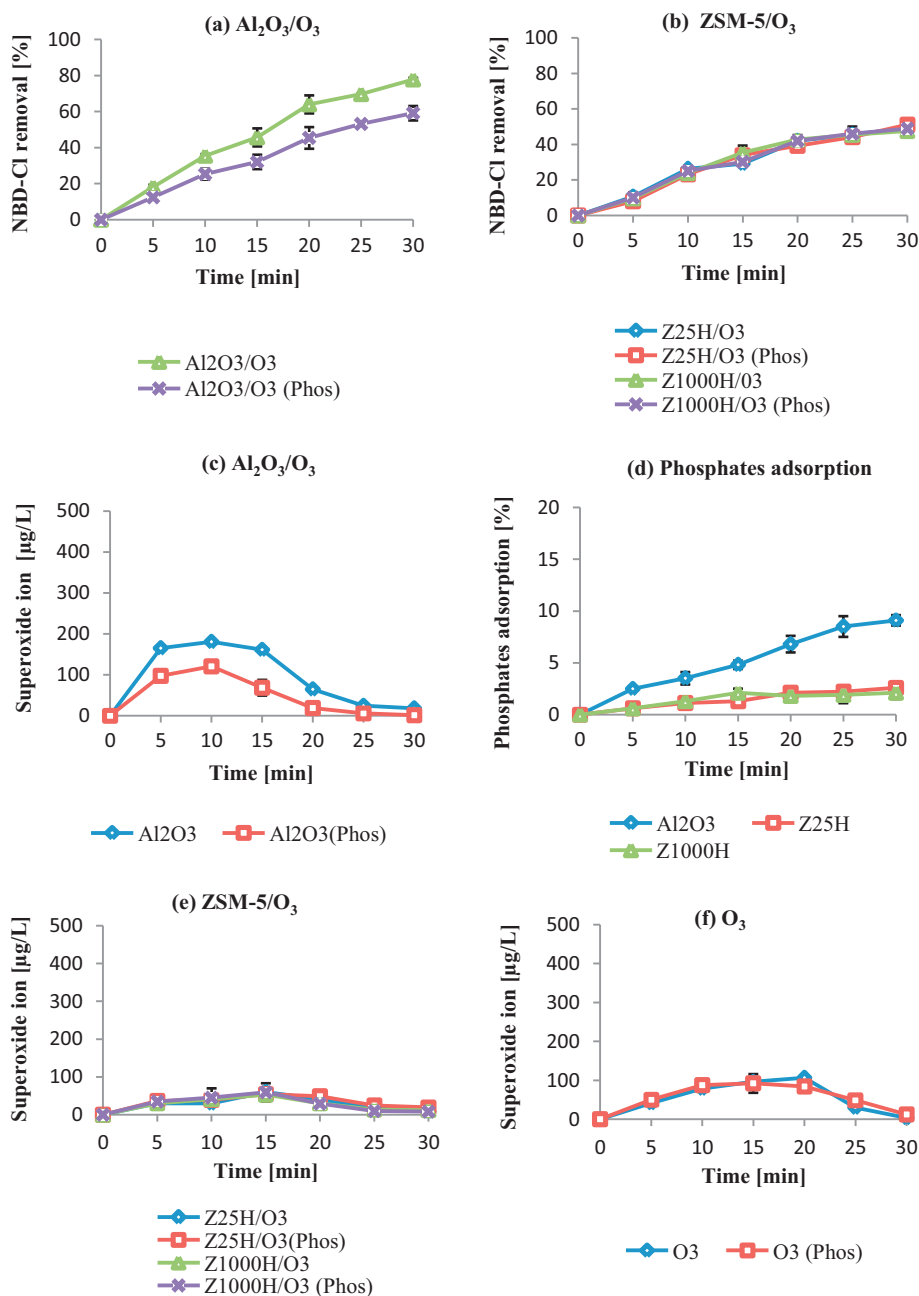
Fig. 7. Effect of phosphates on the removal of NBD-Cl and formation of superoxide ion in O_3, Al_2O_3/O_3 and ZSM-5/O_3 ($C_{o\,(NBD-Cl)}$ = 20 mg/L; O_3 = 0.6 mg/min; T = 25 °C; pH = 8.8; phosphates = 50 mg/L catalyst = 2 g; V = 190 mL; SD ± 5).

of superoxide ion radical $^{o}O_2^{-}$ in the formation of hydroxyl radicals and to investigate the effect of TBA on the removal of NBD-Cl by catalytic ozonation on alumina and HZSM-5 zeolites. The results indicate that the presence of TBA did not have any significant effect on the removal of NBD-Cl in the presence of ZSM-5 zeolites. For example NBD-Cl removal was 50% with and without TBA when HZSM-5 zeolites have been used (Fig. 6c). Furthermore, no significant change in $^{o}O_2^{-}$ concentration was observed in the case of HZSM-5/O_3 zeolites (Fig. 6e) and ozonation alone (Fig. 6f) with or without TBA. This indicates that ZSM-5 zeolites did not generate $^{o}O_2^{-}$ and ^{o}OH radicals.

It has been observed that a small decrease in the removal of NBD-Cl took place in the case of O_3 alone undertaken in the presence of TBA. For example 40% and 35% of NBD-Cl was removed after 30 min ozonation at pH 8.8 when ozonation was conducted

with and without TBA, respectively (Fig. 6a). Similarly, there has been some limited decrease in the NBD-Cl removal (3% after 30 min ozonation time) in the case of ozonation in the presence of alumina when TBA was added to the solution. This may be because of $^{o}O_2^{-}$ scavenger effect of NBD-Cl [12]. It was further suggested that superoxide ion radical plays an important role in the formation of hydroxyl radicals [5]. Therefore, it is hypothesised that in the presence of NBD-Cl formation of $^{o}O_2^{-}$ is restricted, therefore the generation of hydroxyl radicals may be also restricted.

3.1.5. Effect of phosphates

Ozonation experiments in the presence of phosphates were conducted in order to verify the importance of surface hydroxyl groups present on the surface of alumina in ozone decomposition and to understand the possible influence of phosphates on ozonation
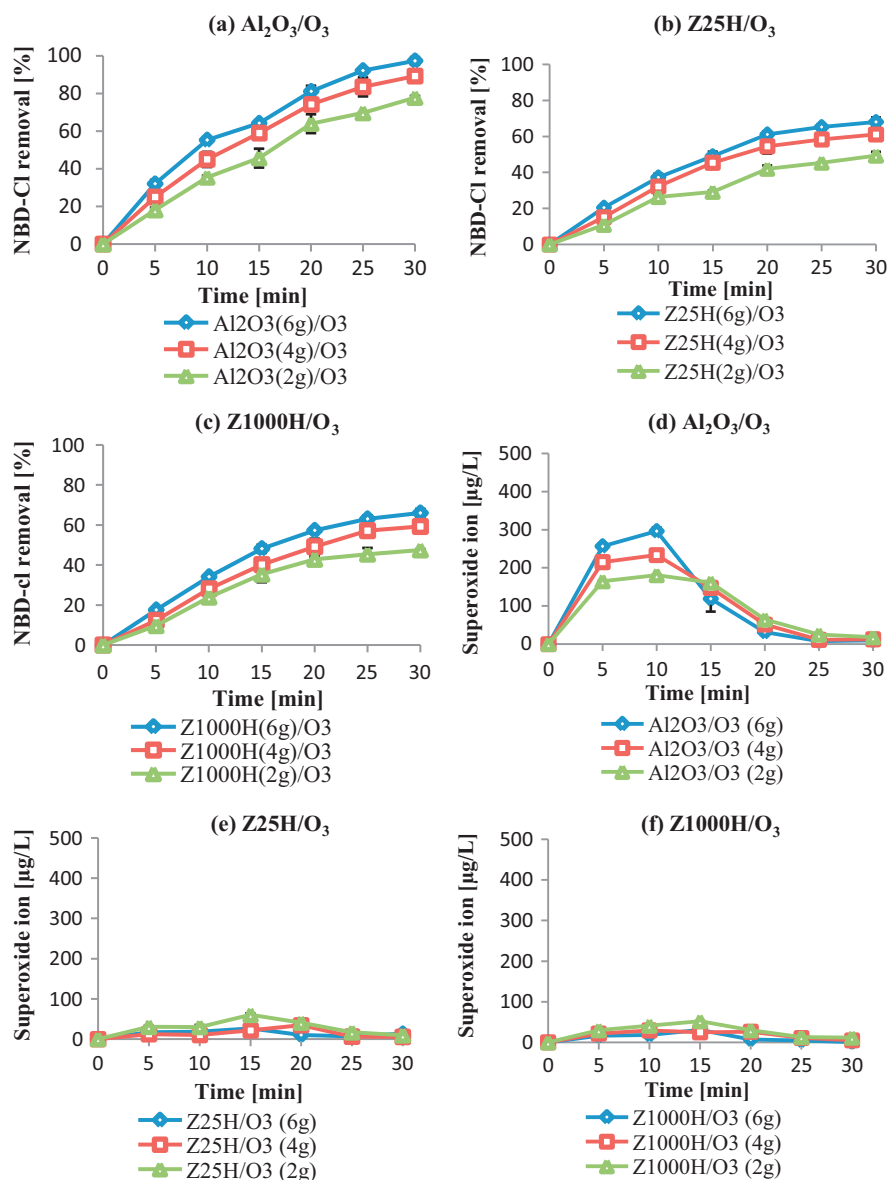
Fig. 8. Effect of catalyst amount on the removal of NBD-Cl and formation of superoxide ion by Al_2O_3/O_3 and HZSM-5/O_3 ($C_{o\,(NBD-Cl)}$ = 20 mg/L; T = 25 °C; pH = 8.8; O_3 = 0.6 mg/min; catalyst amount = 2.0 g, 4.0 g and 6.0 g; V = 190 mL; SD ± 5).

in the presence of ZSM-5 zeolites [27]. The effect of phosphates on the formation of $^oO_2{}^-$ and removal of NBD-Cl was studied in the presence of O_3 alone, ozonation in the presence of HZSM-5 (Z25H and Z1000H) zeolites and alumina at pH 8.8 (Fig. 7). The results presented in Fig. 7b indicate that the presence of phosphates did not have any significant effect on the removal of NBD-Cl in ozonation on HZSM-5 zeolites. Furthermore, no significant change in superoxide ion formation has been observed with or without phosphates in the case of ZSM-5 zeolites (Fig. 7e) and ozonation alone (Fig. 7f). However, the formation of superoxide ion radical was significantly reduced in the presence of phosphates, when ozonation was conducted in the presence of alumina. For example 180.5 μg/L of superoxide has been formed in the case of Al_2O_3/O_3 (in the absence of phosphates) in the first 10 min and it was reduced to 120.5 μg/L of superoxide in the presence of phosphates (Fig. 7c). Furthermore, the NBD-Cl removal percentage was significantly reduced in Al_2O_3/O_3 in the presence of phosphates. For example (at pH 8.8, after 30 min ozonation time) the removal of NBD-Cl was reduced from the initial value (without phosphates) of 80% to 60% (in the presence of phosphates) (Fig. 7b). Similarly to the

results presented in our previous paper [27] the adsorption studies of phosphates on HZSM-5 and alumina (Fig. 7d) revealed that, as expected, at studied conditions (pH 8.8) alumina has much higher adsorption capacity towards phosphates than HZSM-5 (8% on 2 g of alumina and 2% on Z25H and Z1000H, in 30 min). It is suggested that the decrease in $^oO_2{}^-$ formation in the presence of phosphates in the case of Al_2O_3/O_3 is resulting from a decrease of available surface OH groups. As discussed before, interaction of ozone with surface hydroxyl groups results in the formation of $^oO_2{}^-$ [8].

3.1.6. Effect of catalyst amount

In order to study the effect of catalyst amount on the removal of NBD-Cl and formation of superoxide ion radical, HZSM-5 (Z1000H and Z25H) and alumina were selected. Experiments were performed using 2 g, 4 g and 8 g of catalysts in the semi-batch (190 mL of 20 ppm NBD-Cl solution in water) reactor at pH 8.8. The results presented in Fig. 8 show that with the increase in the catalyst amount the NBD-Cl percentage removal increased for both Al_2O_3/O_3 and HZSM-5/O_3. For example ozonation in the presence of 6 g of alumina resulted in the removal of 90% of NBD-Cl in 30 min

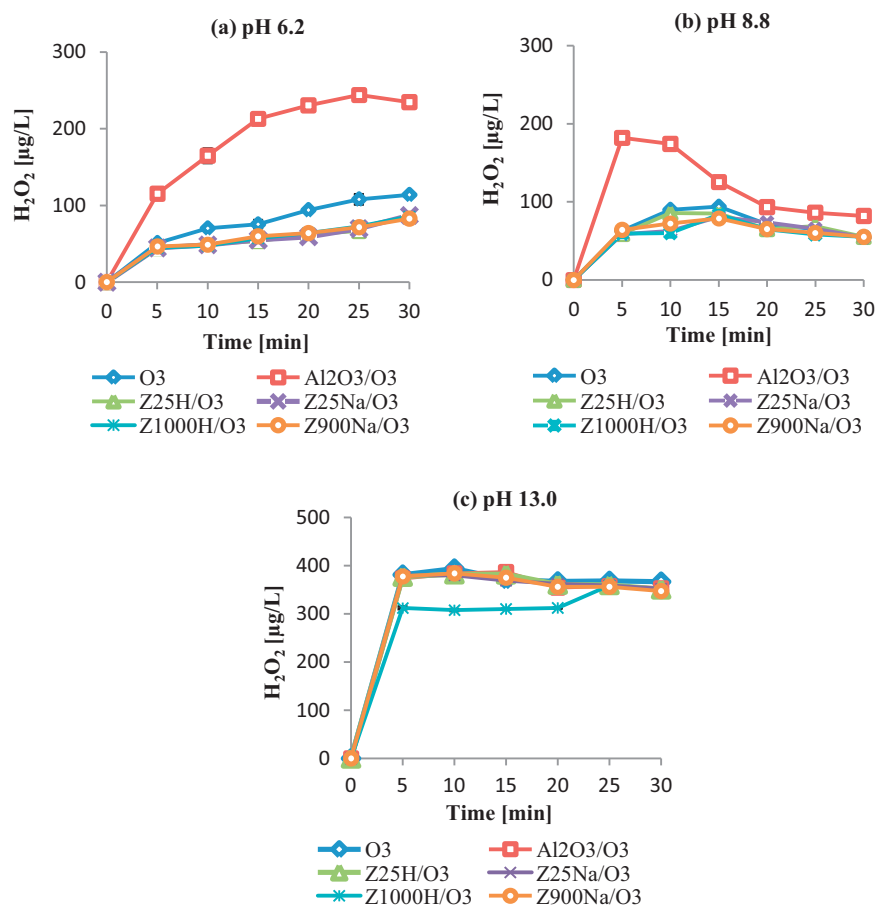**Fig. 9.** Formation of hydrogen peroxide in ozonation alone and catalytic ozonation (C_{oAmp} = 20 mg/L; O_3 = 0.6 mg/min; T = 25 °C; pH = 6.2, 8.8 and 13.0; $pH_{t30\,min}$ = pH ± 0.2; catalyst amount = 2.0 g; V = 190 mL; SD ± 5 µg/L).

and it was only 72% when 2 g of alumina were used (Fig. 8a). It is important to note here, that although the removal of NBD-Cl increased in the presence of HZSM-5 zeolites when the catalyst amount is increased, no significant $^oO_2^-$ formation was observed even at a higher amount. This clearly suggests that ZSM-5 zeolites do not form superoxide ion radicals. In contrast to ozonation on ZSM-5 zeolites, an investigation of $^oO_2^-$ formation revealed that in the case of Al_2O_3/O_3, the concentration of $^oO_2^-$ increases with an increase of the catalyst amount (Fig. 8d). It is worth mentioning here that the increase in $^oO_2^-$ formation was not linear. A sharp increase during the first 10 min of ozonation was observed and then it decreased. Therefore, it is assumed that the NBD-Cl product (an indicator of $^oO_2^-$ formation) might be degraded during the catalytic ozonation. On the other hand no significant increase in $^oO_2^-$ formation was observed in the case of ZSM-5/O_3 (Fig. 8e and f).

3.2. Formation of hydrogen peroxide

3.2.1. Effect of pH

The experiments were performed at pH values 6.2, 8.8 and 13.0 as shown in Fig. 9. The results clearly indicate that high concentrations of H_2O_2 are formed with Al_2O_3/O_3 at both pH 6.2 and 8.8 when compared with ozonation alone. For example, the concentration of H_2O_2 was (at pH 6.2, after 30 min ozonation) 234.5 µg/L for Al_2O_3/O_3 and only 114 µg/L for O_3 alone. It has been reported previously that alumina shows catalytic activity near or below its point of zero charge and when the pH becomes higher, catalytic activity is greatly reduced [18,19,29]. Al_2O_3 catalytic activity is

directly related to its capacity to decompose ozone on its surface hydroxyl groups, which leads to the formation of hydroxyl radicals [18,19,29]. In contrast, at pH 13 the presence of alumina did not result in any increase in H_2O_2 production. It was therefore concluded that H_2O_2 formation in Al_2O_3/O_3 related to ozone decomposition and it was higher at pH 8.8 than 6.2 in the first 5–10 min of ozonation (Fig. 9a and b). This is because the catalytic activity of alumina is the highest near its point of zero charge. Furthermore, it was observed that at pH 6.2 H_2O_2, production was very rapid for the first 10–15 min (Fig. 9a) and then slowed down. This may be due to adsorption and decomposition of H_2O_2 on alumina [30]. It was also observed that at basic pH (Fig. 9b and c), the rate of H_2O_2 formation in the first 5 min was high and then it decreased for both the ozonation and catalytic ozonation processes. This may be because of the low stability of H_2O_2 at basic pH values [5]. Furthermore, H_2O_2 may further adsorb and decompose on the catalyst surface [30]. Additionally, it is hypothesised that resorufin (the product of the reaction between H_2O_2 and amplex red) may be decomposed by the oxidative species (such as ozone and hydroxyl radicals) in the system.

The results for ZSM-5 zeolites clearly indicate that no significant increase in H_2O_2 formation was observed at any pH when compared with ozonation alone. It is therefore assumed that ZSM-5 zeolites mainly act as adsorbents of ozone and do not decompose aqueous ozone leading to the formation of free reactive oxidative species such as hydrogen peroxide or hydroxyl radicals. However, zeolites do catalyse the decomposition of pollutants by direct reaction between adsorbed ozone and pollutants on their surfaces.
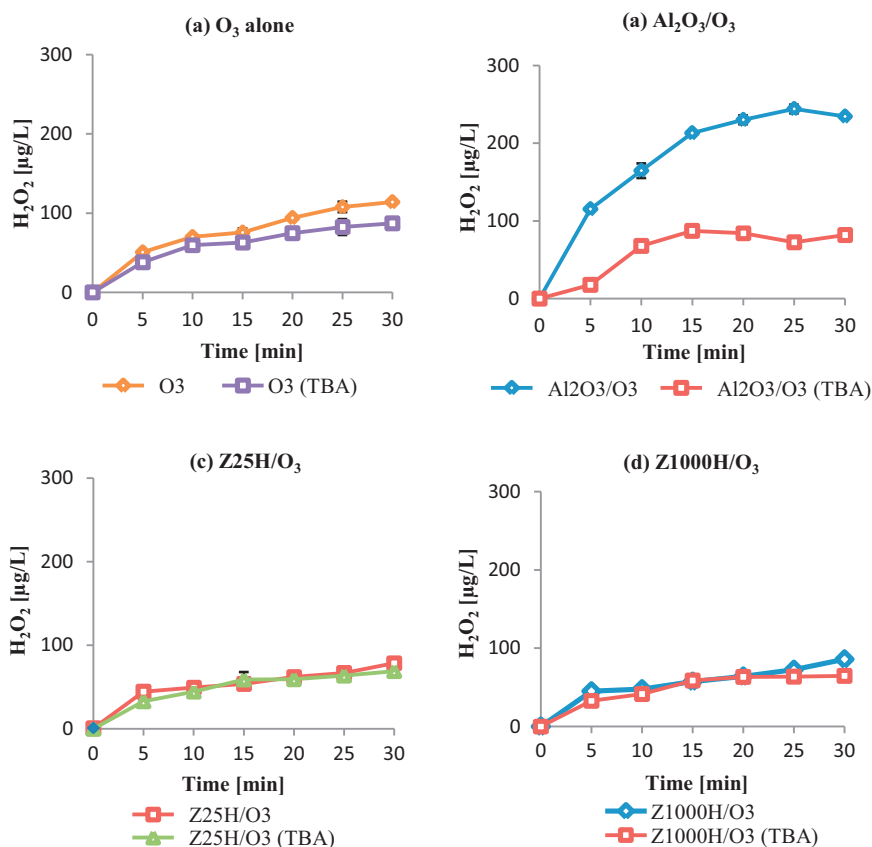
Fig. 10. Effect of TBA on the formation of hydrogen peroxide by O_3, Al_2O_3/O_3 and HZSM-5/O_3 (C_{oAmp} = 20 mg/L; O_3 = 0.6 mg/min; TBA = 50 mg/L; T = 25 °C; pH = 6.2; $pH_{t30 min}$ = 6.2 ± 0.2; O_3 = 0.6 mg/min; catalyst amount = 2.0 g; V = 190 mL; SD ± 4 μg/L).

3.2.2. Effect of TBA

The hydroxyl radicals may combine to form stable H_2O_2 [4,30]. The formation of H_2O_2 in the catalytic ozonation process has been investigated by the use of hydroxyl radical scavengers such as TBA. The results presented in Fig. 10b clearly indicate that in the presence of alumina TBA inhibits the formation of H_2O_2. For example at pH 6.2 after 30 min ozonation time the H_2O_2 concentration was 234.5 μg/L and in the presence of TBA it was reduced to 81.9 μg/L. Furthermore, it was observed that the decrease of H_2O_2 concentration also took place in the case of O_3 alone. As shown in Fig. 10a the concentration of H_2O_2 in ozonation alone was 114 μg/L and was reduced to 87.2 μg/L in the presence of TBA. However, the decrease in H_2O_2 concentration in O_3 alone (in the presence of TBA) was not as great as in the case of Al_2O_3/O_3. This suggests that °OH radicals play an important role in the formation of H_2O_2 and the presence of alumina generates more °OH radicals compared with ozonation alone [18,19,29].

The results presented in Fig. 10c and d show that TBA did not have any effect on H_2O_2 formed in the presence of HZSM-5 zeolites (both Z1000H and Z25H). The amount of H_2O_2 formed in the presence of zeolites was lower than in ozonation alone. It has already been discussed that ZSM-5 zeolites may mainly act as adsorbents of both ozone and organic contaminants and do not lead to the formation of free reactive oxygen species such as hydroxyl radicals and the above results further support this view.

3.2.3. Effect of phosphates

The effect of phosphates on the formation of H_2O_2 was studied with O_3 alone, and in the presence of HZSM-5 (Z25H and Z1000H) zeolites and alumina at pH 6.2 (Fig. 11). The results indicate that the

presence of phosphates did not have a significant effect on H_2O_2 formed during ozonation in the presence of HZSM-5 zeolites. On the other hand, the H_2O_2 concentration was significantly reduced during the ozonation in the presence of alumina after 30 min, from 234.5 μg/L to 101 μg/L at pH 6.2 (Fig. 11b). The presence of phosphates slightly reduced the H_2O_2 formation with O_3 alone (Fig. 11a). This is presumably due to the radical scavenger effect of phosphates. This effect is not seen with HZSM-5 zeolites and this may simply be because of adsorption of phosphates on zeolites, which resulted in the reduction of the concentrations of phosphates in the solution.

The adsorption studies of phosphates on HZSM-5 and alumina (Fig. 11e) revealed that alumina had much higher adsorption for phosphates than HZSM-5 (14.5%, 3.6 mg/g, on 2 g of alumina and 3.4%, 0.9 mg/g, 3.1%, 0.8 mg/g on 2 g of Z25H and Z1000H, respectively, in 30 min). It is therefore suggested that the decrease in H_2O_2 formation in the presence of phosphates in the case of Al_2O_3/O_3 is the result of a decrease in available surface hydroxyl groups. As discussed before, the interaction of ozone with surface hydroxyl groups results in the formation of hydroxyl radicals and these hydroxyl radicals combine to form H_2O_2.

3.2.4. Effect of catalyst amount

The results presented in Fig. 12 show that with an increase in the catalyst amount the concentration of H_2O_2 formed increased in the case of Al_2O_3/O_3. This may be due to the increase in hydroxyl radical formation in line with the increase in catalyst amount, which leads to the formation of H_2O_2. Additionally, it was noticed that H_2O_2 was formed rapidly in the first 10–15 min of ozonation (Fig. 12a).
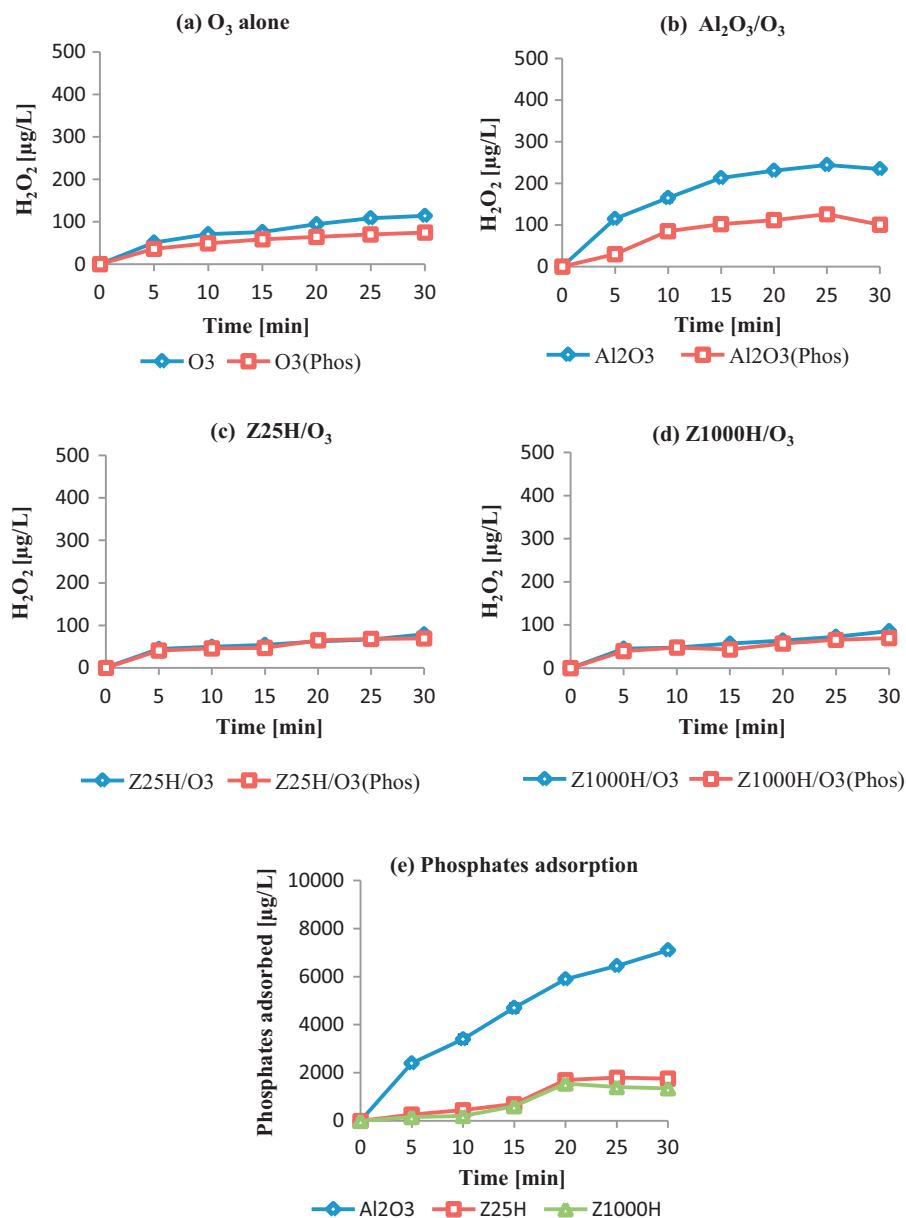
Fig. 11. Effect of phosphates on the formation of hydrogen peroxide in O_3, Al_2O_3/O_3 and HZSM-5/O_3 ($C_{oAmp} = 20$ mg/L; $O_3 = 0.6$ mg/min; phosphates = 50 mg/L; $T = 25\,^{\circ}$C; pH_o, 6.2; $pH_{t30\,min} = 6.2 \pm 0.2$; catalyst amount = 2.0 g; $V = 190$ mL; SD $\pm 10\,\mu$g/L).

This may be due to the adsorption and decomposition of H_2O_2 on alumina.

The experiments conducted in the presence of HZSM-5 zeolites (Fig. 12b and c) indicated that zeolites did not have any effect on the formation of H_2O_2. As discussed before this may be because ZSM-5 zeolites mainly act as adsorbents of ozone and do not initiate the advanced oxidation mechanism that leads to the generation of free reactive oxygen species.

3.3. Proposed mechanisms

The above results are important in explaining the mechanisms of catalytic ozonation. It is certain that alumina promotes the formation of hydroxyl radicals [27], hydrogen peroxide and superoxide ion radical, and it was confirmed using coumarin [27], amplex red and NBD-Cl, respectively, as probe molecules. Additionally, the studies of the TBA effect further support this hypothesis. The mechanism of ozonation in the presence of alumina has been

proposed in Fig. 13. On the basis of the current investigation it is hypothesised that aqueous ozone interacts with the surface hydroxyl groups of alumina which promotes its decomposition and this has been supported by the results of the experiments investigating the phosphates effect. The interactions of aqueous ozone with the surface hydroxyl groups of alumina result in the formation of superoxide ion radical. The formation of superoxide ion during ozonation in the presence of alumina has been confirmed in this work with the NBD-Cl probe and provides strong evidence to support this hypothesis. Furthermore, the decrease in the superoxide ion production in the presence of phosphates further supports this hypothesis. It has been hypothesised by some researchers that the surface hydroxyl groups of catalysts interact with the aqueous ozone leading to the formation of ^oO_2H and superoxide ion radical [7,8,31]. This may be due to the dipole nature of ozone that reacts with the surface hydroxyl groups of catalysts to produce ^oO_2H with the release of O_2. It is further hypothesised that another O_3 molecule reacts with superoxide or

Fig. 12. Effect of catalyst dose on the formation of hydrogen peroxide in O_3, Al_2O_3/O_3 and HZSM-5/O_3 ($C_{oAmp} = 20$ mg/L; catalyst = 2.0 mg/L, 8.0 mg/L; $T = 25$ °C; pH = 6.2; pH$_{t30\,min} = 6.2 \pm 0.2$; $V = 190$ mL; SD ± 4 μg/L).

O_2H^o to produce an ozonide $^oO_3{}^-$ or O_3H^o radical (Fig. 13) [5]. The ^oO_3H radicals quickly reduce to produce hydroxyl radicals. However, this process is pH dependent. At basic pH ^oO_3H exists in the form of its conjugate base $^oO_3{}^-$. Therefore at basic pH $^oO_3{}^-$ reacts with H_2O to produce hydroxyl radicals (Fig. 13) [5]. The formed hydroxyl radicals may combine with one another [4,30] to form

H_2O_2. The stability and formation of H_2O_2 depends upon the pH of the solution and the concentration of hydroxyl radicals. The presence of H_2O_2 has been confirmed in this work by the use of amplex red as a probe molecule. Additionally, the experiments investigating TBA effect clearly indicate that production of hydroxyl radicals is essential for the formation of H_2O_2.

Fig. 13. The mechanism of ozonation in the presence of alumina.

In the case of the zeolite catalysts we found that hydroxyl radicals are not involved in the catalytic ozonation process [27]. Additionally, zeolites do not promote the formation of hydrogen peroxide and superoxide ion radical. However, the zeolites do catalyse the ozonation of organic compounds as clearly seen from the removal of coumarin [27] and NBD-Cl. We propose that the zeolite acts simply as a reactive surface site on which the reaction between O_3 and the organic molecule can take place with reduced activation energy. Within the family of ZSM-5 zeolites the activity of zeolites is directly related to the silica to alumina ratios. The evidence for this suggestion is strong, as indicated by their adsorption and removal of probes. The study of TBA effect further supports this hypothesis. The fact that the hydrogen and sodium forms of the zeolite behave similarly suggests that surface acid sites are not involved in the ozonation reactions.

4. Conclusions

The overall conclusions of this work are as follows:

1. Different mechanisms govern aqueous ozone reactions in catalytic ozonation on alumina and on ZSM-5 zeolites.
2. Ozone decomposition on alumina occurs via radical chain reactions involving the formation of active oxygen species such as ^oOH and $^oO_2^-$. Ozone decomposition takes place as a result of its interaction with surface hydroxyl groups of alumina. This process is pH dependent with the highest formation of ROS at $pH = pH_{PZC}$. Furthermore, natural water constituents such as phosphates can inhibit catalytic decomposition of ozone.
3. ZSM-5 zeolites do not facilitate ozone decomposition but act as ozone reservoirs. Adsorption of ozone and organic molecules on the surface of zeolites is the determining step of the catalytic process. However, ZSM-5 zeolites are effective in the catalytic ozonation of NBD-Cl but they do not act via a radical mechanism. Their activity arises through their ability to adsorb ozone and probes and to promote a surface reaction between the two molecules.
4. The activity of zeolites is independent of the nature of counter ions and their acidity.

Acknowledgments

References

[1] B. Legube, N. Karpel Vel Leitner, Catalysis Today 53 (1999) 61–72.
[2] B. Kasprzyk-Hordern, M. Ziółek, J. Nawrocki, Applied Catalysis B: Environmental 46 (2003) 639–669.
[3] J. Nawrocki, B. Kasprzyk-Hordern, Applied Catalysis B: Environmental 99 (2010) 27–42.
[4] J. Staehelin, R.E. Buehler, J. Hoigne, The Journal of Physical Chemistry 88 (1984) 5999–6004.
[5] J. Staehelin, J. Hoigne, Environmental Science and Technology 16 (1982) 676–681.
[6] W.H. Glaze, J.-W. Kang, D.H. Chapin, Ozone: Science and Engineering 9 (1987) 335–352.
[7] T. Zhang, J. Ma, Journal of Molecular Catalysis A: Chemical 279 (2008) 82–89.
[8] M. Ernst, F. Lurot, J.-C. Schrotter, Applied Catalysis B: Environmental 47 (2004) 15–25.
[9] P.M. Alvárez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, Carbon 44 (2006) 3102–3112.
[10] L. Zhao, J. Ma, Z. Sun, H. Liu, Applied Catalysis B: Environmental 89 (2009) 326–334.
[11] T. Zhang, P. Hou, Z. Qiang, X. Lu, Q. Wang, Chemosphere 82 (2011) 608–612.
[12] R.O. Olojo, R.H. Xia, J.J. Abramson, Analytical Biochemistry 339 (2005) 338–344.
[13] M.I. Heller, P.L. Croot, Analytica Chimica Acta 667 (2010) 1–13.
[14] M. Zhou, Z. Diwu, N. Panchuk-Voloshina, R.P. Haugland, Analytical Biochemistry 253 (1997) 162–168.
[15] N. Soh, Analytical and Bioanalytical Chemistry 386 (2006) 532–543.
[16] G. Bartosz, Clinica Chimica Acta 368 (2006) 53–76.
[17] B. Kasprzyk-Hordern, U. Raczyk-StanisÅawiak, J. Åšwietlik, J. Nawrocki, Applied Catalysis B: Environmental 62 (2006) 345–358.
[18] F. Qi, Z. Chen, B. Xu, J. Shen, J. Ma, C. Joll, A. Heitz, Applied Catalysis B: Environmental 84 (2008) 684–690.
[19] F. Qi, B. Xu, Z. Chen, J. Ma, D. Sun, L. Zhang, Separation and Purification Technology 66 (2009) 405–410.
[20] J. Lin, A. Kawai, T. Nakajima, Applied Catalysis B: Environmental 39 (2002) 157–165.
[21] B. Kasprzyk-Hordern, P. Andrzejewski, A. Dąbrowska, K. Czaczyk, J. Nawrocki, Applied Catalysis B: Environmental 51 (2004) 51–66.
[22] C. Cooper, R. Burch, Water Research 33 (1999) 3695–3700.
[23] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, Water Research 38 (2004) 159–165.
[24] N.A.S. Amin, J. Akhtar, H.K. Rai, Chemical Engineering Journal 158 (2010) 520–527.
[25] V.S.R. Rajasekhar Pullabhotla, S.B. Jonnalagadda, Industrial and Engineering Chemistry Research 48 (2009) 9097–9105.
[26] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, Water Research 38 (2004) 166–172.
[27] A. Ikhlaq, R. Brown, B. Kasprzyk-Hordern, Applied Catalysis B: Environmental 123–124 (2012) 94–106.
[28] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, Standard Methods for the Examination of Water and Wastewater, 21st ed., APHA/AWWA/WEF, 2005.
[29] L. Chen, F. Qi, B. Xu, Z. Xu, J. Shen, K. Li, Water Science and Technology 6 (2006) 43–51.
[30] M. Suh, P.S. Bagus, S. Park, M.P. Rosynek, J.H. Lunsford, The Journal of Physical Chemistry B 104 (2000) 2736–2742.
[31] T. Zhang, C. Li, J. Ma, H. Tian, Z. Qiang, Applied Catalysis B: Environmental 82 (2008) 131–137.